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Synthesis of solvothermal derived TiO_2 nanocrystals supported on ground nano egg shell waste and its utilization for the photocatalytic dye degradation

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ABSTRACT

TiO_2 nanoparticles with excellent crystallinity were synthesized via solvothermal method and supported on the ground nano-sized egg shell waste at different loading concentrations. The photocatalytic degradation of the mixture of Methylene blue (MB) and Rhodamine 6G (Rh 6G) in aqueous solution utilizing prepared TiO_2 nano composite under visible light irradiation was analysed. Different characterizations including UV–Visible (UV–Vis) spectroscopy, Field emission scanning electron microscopic (FE-SEM), energy dispersive studies (EDS), Transmission electron microscopy (TEM) were performed to investigate the physicochemical properties of the prepared catalyst. In addition, FE-SEM and EDS analysis of the prepared egg shell support were carried out to confirm the morphology, particle size distribution, and composition. The solvothermal derived TiO_2 nanocrystals supported on ground nano-sized egg shell waste exhibited enhanced photocatalytic activity as compared to the as-prepared TiO_2 nanoparticles. The synergistic effect of TiO_2 nanoparticles and nano egg shell support is attributed to the effective dispersion of TiO_2 that offers high specific surface area.

1. Introduction

TiO_2 is a wide and intrinsic band gap polymorphic semiconductor material that exists in three distinct mineral phases i.e. anatase, rutile and brookite. TiO_2 nanoparticles have wide range of applications as an efficient optical material such as in heterogeneous catalysis, solar energy conversion, solar cells and fabrication of optical-electronic devices [1–3]. The overall properties of nano sized TiO_2 as photocatalyst depend on many factors such as crystallinity, stability, agglomeration tendency, exposed surface area, morphology and synthesis method [4]. Nanostructured material exhibits unique physical and chemical properties as compared to their micro and bulk counterparts. TiO_2 nanoparticles possess attractive photon detection capability due to their large surface-to-volume ratios and increased active sites [5]. Differences in lattice structures cause different properties between the anatase and rutile forms of TiO_2. For TiO_2 nanoparticles, phonon modes increase with decreasing particle size [6]. A number of methods for TiO_2 nanopowder/nanorods/nanosheets preparation have been reported, such as sol-gel [7], hydrothermal method [8], mechanochemical method [9], oxidation, sonochemical and microwave assisted methods.

Solvothermal synthesis is a method for preparation of various ceramics, polymers and semiconductors using solvent under moderate to high pressure (typically between 1 atm and 10,000 atm) and temperature (typically between 100 °C and 1000 °C). Solvent at that condition facilitates the interaction of precursors during the synthesis process. Solvothermal methods have the capability to synthesize crystalline metal oxides with high purity and morphological control due to high temperature and pressure effect in an enclosed space. Moura et al. [10] synthesized TiO_2 with anatase phase by a microwave assisted solvothermal method without using any templates or alkalinizing agents. TiO_2 nanocrystals with highly exposing ratio of {001} facets with superior photoactivity have been prepared by Cao et al. [11] using

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solvothermal method. Kathirvel et al. [12] obtained rod shaped TiO_2 nanocrystals by simple solvothermal approach without using any surfactants or capping agents.

TiO_2 is a highly stable and UV photoactive semiconductor material. However, drawbacks of using TiO_2 as a photocatalyst include rapid recombination of electron-hole pairs and inability to utilise visible light of the solar spectrum. Therefore, it is desirable to synthesize a solar photoactive TiO_2 that can be used efficiently. Doping of other metals can change the structural and optical properties of TiO_2. Hreniak et al. [13] synthesized Fe doped TiO_2 catalyst that activates with solar irradiation. Among other documented methods to enhance the photoactivity of TiO_2, addition of support or co-sorbent such as SiO_2 [14], zeolite [15] and activated carbon (AC) [16] has attained much attention due to their cost effectiveness and simple procedure. Naeem and Ouyang [17] studied the photocatalytic effect of SiO_2, AC and zeolite mixed physically with TiO_2 and also compared the photo efficiency by using cheaper rice husk as support. In this present study, we have used egg shell powder as support material.

Hens' eggs are used by food manufacturers and the shells are discarded as waste. Therefore, for the best utilization of the egg shell waste, various researches have been conducted. Eggshell has been explored for different applications such as abrasives and adsorbent for many metal ions and organic dyes. It has been investigated that it contains a high level of calcium carbonate and may be used as fertilizer and food additives for livestock [18–20]. Millal et al. [21] reviewed the application of egg shell and egg shell membrane as adsorbents. Elkady et al. [22] utilized eggshell biocomposite beads for the potential removal of reactive red dye.

Heterogeneous photocatalysis is an emerging advance oxidation process for the effective removal of organic contaminants in water and air [23]. Until date, very less work has been reported to the best of our knowledge on using ground egg shell waste as co-sorbent or support with the photocatalysts to increase their activity.

In the present research, solvothermal method was used to synthesize TiO_2 nanoparticles with highly crystalline structure and was further supported on ground nano sized egg shell waste to achieve enhanced photoactivity of the prepared nano catalyst.

2. Experimental

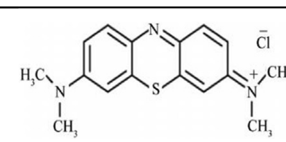
2.1. Materials

Tetrabutyl Orthotitanate (TCI) and absolute ethanol were used for the synthesis of TiO_2. Hen egg shells were collected from discarded waste. Methylene blue and Rhodamine 6G were obtained from market. Properties and structure of the dyes utilized in the dye degradation experiments are shown in Table 1. All the chemicals were of analytical grade and were not purified further.

2.2. Synthesis of TiO_2 nanoparticles

TiO_2 nanoparticles were synthesized via solvothermal method. The pilot plant had been developed in CSIR-Central Institute of Mining and Fuel Research, Digwadih Campus, Dhanbad Jharkhand, India as shown in Fig. 1. An Autoclave had a stainless steel (SS 316) material of construction with 2 L internal volume supplied by Autoclave Engineers, USA, withstand a pressure up to 227 bar at 454 °C. An autoclave was utilized as a reactor in this experiment. It was equipped with temperature sensor [Type K thermocouple (°C)] and pressure sensors. The vessel was heated by means of PID controlled external electric heater. Autoclave was provided with magnetically driven Dispersimax impeller for mixing of reactants which can rotate up to 3300 rpm through panel mounted variable frequency drive controller. Bottom flush valve was provided for product discharge and for cleaning purpose. Rupture disc with safety head and safety relief valve had been mounted. Back pressure regulator was mounted for maintaining desired pressure inside the autoclave. CO_2 has been fed from standard CO_2 cylinder having pressure up to 150 kg/cm^2 through valve 1 (V1) and precursor solution through valve 2 (V2) into the reactor. A back-pressure valve (V4) was used to keep the pressure constant during the continuous process. The TiO_2 obtained was collected at the end of each operation at the bottom of the reactor through bottom flush valve (V6). All valves were rated at 425 °C and pressure up to 340 kg/cm^2. P1, P2 and P3 designates CO_2 regulator pressure (0–150 bar), reactor pressure (0–250 bar) and back pressure valve (0–350 bar) respectively. In a typical procedure, tetrabutyl Orthotitanate (372 ml) was added to 583 ml ethanol and 45 ml distilled water and charged into the reactor through valve V2. CO_2 was fed to the reactor through gas sparger until the work pressure was attained i.e. 80 bar, shown by P2. The system was heated up until the desired reaction temperature i.e. 55 °C was reached using PID controllers. Inside temperature of the reactor was measured through additional thermocouple mounted inside thermo-well and indicator. For all the experiments stirrer rpm was maintained 500 rpm to obtain uniform mixing of the reactants. Finally, after the residence time of 10 h, the product mass was collected through valve V6 and washed with distilled water and ethanol several times. Next step of the process aimed to remove excess water and ethanol from the recovered product. Thus, the product was filtered using vacuum filtration and dried at 100 °C in a hot air oven for 2 h. The as-prepared solvothermal method derived TiO_2 nanoparticles were designated as TS.

Table 1
Properties and structure of the organic dyes utilized for the dye degradation experiments.

Chemical name	Chemical formula	Nature	λ_{max} (nm)	Molecular weight(g/mol)	Molecular Structure
Methylene blue	$C_{16}H_{18}ClN_3S$	Cationic	664	319.85	
Rhodamine 6G	$C_{28}H_{31}N_2O_3Cl$	Cationic	522–527	479.02